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IN-SITU SPECTROSCOPIC STUDIES OF REDOX ACTIVE SELF-ASSEMBLED
MONOLAYERS ON GOLD ELECTRODE SURFACES

by

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The spectra also displayed two strong negative-going peaks in the region between 2800 and 3000 cm^{-1} . This can be explained on the basis that the alkyl chains in the dication are in a collapsed (or unstretched) form adopting a more stretched configuration (with the skeletal axis pointing away from the surface) when in the reduced state, leading to a net decrease in the C-H stretching contribution to the spectra.



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**IN SITU IR SPECTROSCOPIC STUDIES OF REDOX ACTIVE SELF-ASSEMBLED MONOLAYERS
ON GOLD ELECTRODE SURFACES**

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ABSTRACT

Monolayers of N-ethyl-N'-octadecyl-4,4'-bipyridinium (EOB) have been prepared on smooth gold surfaces prepared by spontaneous self-assembly of the electrochemically reduced form of the amphiphile and have been examined with in situ Fourier Transform Infrared Reflection Absorption Spectroscopy (FTIRRAS). Prominent positive-going peaks with hardly any detectable negative-going counterparts were observed in the normalized potential difference spectra of the layer in the reduced state (using as a reference the spectra for the layer in the fully oxidized state) in the region between 1100 and 1700 cm^{-1} . In analogy with a model put forward by other workers it is proposed that the spectral bands originate from vibronically activated totally symmetric modes of EOB^+ in monomeric and/or dimeric form. The large intensity of these vibronically based charge oscillations suggests that at least in the reduced state the plane of the bipyridinium moiety is close to parallel to the electrode surface. An alternate explanation based on a molecular reorientation induced by changes in the redox state was also considered. Such a model, however, was discarded as it fails to account for the large differences in the intensities of the positive- and negative-going peaks observed for solution phase FTIR spectra of the closely related N,N'-dimethyl-4,4'-bipyridyl species.

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INTRODUCTION

Self-assembled monolayers containing redox active centers represent a unique type of organized two-dimensional structures, in that the absolute surface concentrations can be determined from conventional coulometric analyses.¹⁻³ Some of these layers exhibit remarkably high stability to repetitive potential cycling over a substantial voltage range. This affords ideal conditions for acquiring detailed information regarding modifications in the vibrational and electronic properties of the layer induced exclusively by the externally applied potential. The latter may include changes associated with characteristic features of the redox site(s) as well as possible conformational rearrangements within the layer itself.

This paper presents the results of in situ potential difference Fourier Transform Infrared Reflection Absorption Spectroscopy (FTIRRAS) for self-assembled layers of N-ethyl-N'-octadecyl-4,4'-bipyridinium (see Inset Figure 1), denoted hereafter as EOB, on gold surfaces in aqueous solutions. EOB, as well as the methyl substituted analog, may be regarded as model systems of a much wider variety of redox active amphiphiles and as such appear especially suited for these studies.

The experimental approach employed in this work has followed very closely that described by Sasaki et al.⁴ to monitor modifications in the vibrational properties of 2,5-dihydroxythiophenol irreversibly adsorbed on Au and Pt surfaces engendered by changes in the redox state.

EXPERIMENTAL

The bromide salt of EOB was synthesized according to procedures reported in the literature.⁵ It was then purified by recrystallization from DMF and then characterized with NMR, IR and cyclic voltammetry. The in situ electrochemical cell for FTIRRAS measurements as well as the electrochemical

and spectroscopic instrumentation have been described elsewhere.^{4,6} Both a CaF_2 prism and a flat ZnSe window were used in the experiments.

Exposure of the bare gold electrode to a solution 0.05 mM EOB in 0.5 M Na_2SO_4 either at open circuit or at 0.0 V vs SCE yielded very small redox peaks at a potential of about -0.48 V. Considerably enhanced voltammetric features with charges consistent with the presence of a monolayer of adsorbed material could be observed either by cycling between 0.2 and -0.7 V, or simply by holding the potential at the most negative limit for a short period of time. This suggests that the self-assembly of the layer is facilitated when the EOB species is present in the reduced state. Layers formed in this fashion displayed remarkable stability. This was evidenced by the fact that no detectable losses in the area under the voltammetric peaks could be observed even after extensive potential cycling in a region encompassing the redox features.

For the FTIRRAS spectroscopic experiments, the layer was formed directly in the spectroelectrochemical cell by potential cycling. The EOB containing solution was drained and the cell washed (three times) and later filled with neat supporting electrolyte. A cyclic voltammogram was then recorded in order to determine the number of redox active species with the electrode pulled away from the optical window. Subsequently, the electrode was pushed against the window and the spectral acquisition was initiated.

Two closely related techniques were used in order to collect the potential difference FTIRRAS spectra using in both cases the spectrum of the layer in the fully oxidized state (-0.3 V) as the reference. In the single potential step method a large number of scans (> 200) is recorded at one potential, E_1 . After the acquisition is completed the electrode is polarized at a different potential, E_2 , and an equal number of scans is accumulated. In the other method, FTIRRAS spectra at the two same potentials is recorded

in an alternate fashion until an optimized signal to noise ratio is achieved. Regardless of the specific technique used, the final spectra are displayed in terms of $-\Delta R/R$ ($= [R(E_1) - R(E_2)]/R(E_1)$) vs wavenumber, where $R(E_2)$ represents the spectrum at the potential E_2 , with that at E_1 assumed to be the reference.

RESULTS AND DISCUSSION

I. Electrochemistry

Typical cyclic voltammetric curves obtained for a self-assembled layer of EOB prepared in the fashion described in the experimental section in a solution 0.5 M Na_2SO_4 are shown in Figure 1. The redox peaks observed at about -0.47 V are in good agreement with those reported by Díaz and Kaifer in the same electrolyte with the EOB present in the solution using Pt and Au electrodes.² These are also in accordance with those reported by Widrig and Majda in 0.1 M KCl for the closely related N-methyl-N'-octadecylbipyridinium denoted hereafter as MOB.³

The coverage of EOB obtained by integration of the voltammetric peak yielded values of about $2.7 \cdot 10^{-10} \text{ mol} \cdot \text{cm}^{-2}$, and thus less than half those reported in Ref. 2. This discrepancy, however, may be associated with differences in the degree of roughness of the electrodes used and the presence of EOB in the electrolyte in the cited work. In fact, for the case of self-assembled monolayers of MOB adsorbed on vapor deposited Au on glass substrates, Widrig and Majda report saturation coverages of 2.0 and $4.0 \cdot 10^{-10} \text{ mol} \cdot \text{cm}^{-2}$ for electrolytes involving different types of ions.³ On the basis of the similarities between the results obtained in this work and those in Ref. 3, the length of one of the alkane chains does not seem to affect the overall electrochemical properties of the self-assembled layer. Voltammetric measurements in which small amounts of sulfuric acid or NaOH

were added to the base sulfate electrolyte indicated that the potential of the redox feature is independent of pH over the range between 4 and 9. Since protons are not involved in the redox process the changes in pH in the thin layer of electrolyte trapped between the electrode and the window during the FTIRRAS experiments can be regarded as negligible.

II. In situ Fourier Transform Infrared Reflection Absorption Spectroscopy

A series of potential difference FTIRRAS spectra obtained in the potential range in which EOB undergoes changes in the redox state are given in Figure 2. As indicated, the reduction of the self-assembled monolayer gives rise to the appearance of several clearly defined positive-going peaks in the region between 1100 and 1700 cm^{-1} (shown in expanded form in Figure 3), two negative-going peaks at 2854 and 2926 cm^{-1} and some additional features of much lower intensity. Essentially identical spectra were obtained by coadding alternate FTIRRAS spectra at -0.3 V and -0.65 V, which correspond to potentials at which the layer exists in distinct oxidation states (see Curve B, Figure 4).

In accordance with the conclusions put forward on the basis of the electrochemical data (*vide supra*), no desorption of the material could be detected spectroscopically. This is clearly shown by the featureless character of the spectrum obtained at -0.3 V after collecting the spectra at the more negative potentials (see top curve in Figure 2).

Spectral Assignments

The spectroscopic properties of asymmetrically N,N'-substituted 4,4'-bipyridinium ions and their singly reduced counterparts have been found to be consistent with those belonging to a D_{2h} group, despite their lower symmetry.⁷ If it is assumed that the species in the self-assembled monolayer also retain a D_{2h} character, at least two possible models can be proposed to explain the in situ FTIRRAS results obtained in this work.

A. Molecular Reorientation

A detailed comparative analysis of the normal modes associated with the dication and monocation radical forms of N,N'-dimethyl-4,4-bipyridinium, DMB^{2+} appears to be available only for modes of a_g symmetry (see Table I).^{8,9} As these data show, the shifts in the position of the corresponding features for the two species are rather small. Hence, if it is assumed that the more complete analysis reported for the dication is also valid for the radical, the spectral features in Figure 3 at 1640 and 1335 cm^{-1} may be attributed to B_{2u} modes and those at 1597, 1508 and 1192 cm^{-1} to b_{3u} modes.^{8,9} It may be noted that three of these bands (1597, 1335 and 1026 cm^{-1}) are not observed in the spectrum of EOB obtained in the solid state. Although agreement has been reached regarding the detailed assignments of most normal modes, the controversy surrounding the feature at about 1200 cm^{-1} appears to remain still unresolved. For example, Hester and coworkers, in their more recent work,⁸ have attributed this mode to a ring breathing vibration, whereas Cotton and coworkers,^{7,9} have concluded, based on the splitting of this feature induced by an asymmetric N,N'-substitution of the bipyridyl moiety, that this band contains significant contribution from the N-alkyl stretching vibration. This uncertainty is most unfortunate as it precludes a more precise determination of the mode of bonding of the quasi planar moiety to the surface.

Irrespective of this controversy, the fact that the spectra display only positive-going bands can in principle be ascribed to a reorientation of the bipyridinium upon reduction involving a significant increase in the angle formed between the molecular plane and the electrode surface compared to that prevailing in the oxidized state. If it is further assumed that the assignment suggested by Cotton and coworkers^{7,9} is correct, the reduction of

the bipyridyl fragment would be accompanied by a large increase in the angle formed between the long (rather than the short) axis of bipyridyl and the electrode surface. In disagreement with this specific configurational change is the fact that the prominent solid state band at ca. 831 cm^{-1} (attributed by both research groups to the N-alkyl group) is not found in the in situ spectra.

Although a reorientation model would seem at first to be consistent with many of the experimental observations, it fails to account for the spectral behavior of solution phase species of closely related compounds reported by other authors.^{10,11} This points to a different physical phenomenon as responsible for these unique effects.

B. Vibronic Coupling

Spectra displaying features very similar to those in Figure 3 have been reported by Christensen and Hamnett¹⁰ for solution phase DMB^{2+} in aqueous electrolytes using an in situ potential difference FTIR technique analogous to that described in the experimental section (see Table I). In striking analogy with the results shown in Figure 3, only positive-going features could be clearly detected by these authors. This effect is particularly noticeable for the case of the band at ca. 1200 cm^{-1} , which is the most intense feature both for DMB^{2+} and $(\text{DMB}^+)_2$. This suggests that the much stronger signals associated with the monocation are intrinsic to that species and not the result of a molecular reorientation.

As suggested by Christensen and Hamnett,¹⁰ the most likely explanation for this phenomenon may be found in vibronically coupled charge oscillations.¹² Such electronic vibrations are believed to be responsible for the activation of A_g modes in the IR spectra, and under certain conditions can lead to extraordinary enhancements in the magnitude of the absorption.¹³

Among the better studied compounds for which this phenomenon is particularly prominent are the alkali metal salts of tetracyanoquinodimethane (TCNQ) in the solid state, and especially TCNQ stacks composed of dimers for which the charge oscillations are expected to occur along an axis perpendicular to the TCNQ planes.¹⁴

With the possible exception of a band at about 1255 cm^{-1} , for which the intensity may be too small to be detected in the FTIRRAS spectra of the self assembled EOB layer, there exists good agreement between the theoretical and observed A_g features for the closely related (DMB⁺) and those in Figure 3 (see Table I). As suggested earlier in the literature,⁷ the features at 1508 and 1597 cm^{-1} appear to be associated with a dimeric form of the monocation and are particularly prominent in the FTIR spectra of solution phase (DMB⁺) reported in Ref. 10. Also attributed to dimers is a band at 1026 cm^{-1} observed in similar FTIRRAS spectra (not shown in this work) involving a flat ZnSe optical window. Unfortunately it is not possible based on the information available to determine the extent to which dimerization occurs.

According to Devlin and coworkers,¹³ the vibronic activation of totally symmetric modes can be brought about by charge transfer to a counter ion, present either in the crystal or in solution (ion-pair) and therefore the mere observation of the effect may not be used as proof of dimer formation. In fact, for the case of the sodium salt of tetracyanoethylene, Na_3TCNE ¹³ (for which large enhancements in the intensity of vibronically coupled modes have been observed upon cooling the specimens from room down to cryogenic temperatures, ca. 90K) the formation of dimers seems unlikely because of unfavorable electrostatic interactions between the highly charged anions.

Regardless of the role dimers or ion pairs may play in the observed enhancement, the selection rules for surface IR on electronic conductors

would suggest that for the self-assembled singly-reduced EOB monolayer, the axis perpendicular to the bipyridyl ring planes forms a small rather than a large angle with respect to the normal to the electrode surface.^{14e} In fact, similar arguments have been invoked by Pons and coworkers¹⁵ to explain the appearance of A_g IR forbidden bands in their subtractively normalized interfacial FTIR spectra of tetracyanoethylene TCNE radicals on Pt surfaces. In that case, however, a monomeric (rather than a dimeric) species was assumed to lie with the plane parallel to the electrode surface.

This nearly flat configuration would be at variance with that proposed by Widrig and Majda³ for MOB on the basis of electrochemical and Langmuir-Blodgett film measurements, who postulated that the bipyridinium heads are adsorbed on the surface with the long axis perpendicular to the electrode surface.

A second remarkable aspect of the in situ FTIRAS spectra is the presence of the strong negative-going peaks at 2926 and 2856 cm^{-1} (and also the much less pronounced band at 1458 cm^{-1}) associated with asymmetric ν_a , and symmetric ν_s $-\text{CH}_2-$ modes of the alkyl chains, respectively (see Figure 2). One possible explanation for this effect may be found in conformational changes of the self-assembled units that render a much larger fraction of C-H bonds with finite projections along the axis normal to the electrode surface in the oxidized compared to the reduced state. This situation would arise if one (or both) of the alkyl chains would adopt upon reduction and/or further dimerization of the redox centers a stretched configuration in which the skeletal axis would be normal to the surface. Although no distinctions could be inferred by Widrig and Majda³ between the oxidized and reduced configurations, the alkyl chains in their view, were assumed to point away from the electrode surface.

Such conformational modifications induced by the viologen-centered redox process may be caused by the expulsion (reduction) or incorporation (oxidation) of counterions into the layer to preserve electroneutrality. Direct evidence for ionic migration into and out of closely related thiol-linked alkyl-viologen self assembled layers has been obtained by De Long and Buttry using quartz crystal microbalance techniques.¹⁶

III. Spectroelectrochemical Characterization of EOB Oxidation

After the experiments had been completed, an attempt was made to obtain the absolute spectra of adsorbed EOB. To this end, a spectrum was first acquired with the electrode polarized at -0.3 V. The potential was then stepped to +1.5 V, kept at this potential for 30 min. and then returned to -0.3 V at which point a new spectrum was collected. As shown in Figure 5, the FTIRRAS spectra using as a reference the original spectrum yielded a number of clearly defined negative going peaks which may be attributed to the fraction of original EOB material in the oxidized state which was electrochemically oxidized by exposure to the high potential. A simple inspection of the atomic displacements associated with each of the modes and the selection rules for reflection absorption IR on high electronic conductors provides clear evidence that the plane of the bipyridinium ring forms a finite angle with respect to the plane of the surface.

As the positive going peak at 2343 cm^{-1} suggests, the oxidation of EOB as well as a wide variety of organic species,¹⁷ yields carbon dioxide as one of the products.

SUMMARY

The changes in oxidation state of self-assembled monolayers of N-ethyl-N'-octadecyl-4,4'-bipyridinium, EOB, have been monitored with in situ

Fourier Transform Infrared Spectroscopy. Although a model based on a reorientation of the bipyridyl rings induced by changes in the redox state could account for much of the spectral behavior observed, it fails to provide a satisfactory explanation for the disparate intensities of similar in situ FTIRRAS spectra for aqueous solutions of the closely related N,N'-dimethyl-4,4'-bipyridinium. As has been proposed by other authors, the results obtained indicate that upon reduction the EOB undergoes either dimerization or otherwise interacts electronically with the electrode surface or other ions in the solution giving rise to vibronically coupled allowed modes which are IR forbidden. Based on the high intensity of the (positive-going) bands in the normalized FTIRRAS spectra for the reduced species using as a reference the spectrum obtained for the layer in the oxidized state, the bipyridinium plane for the reduced species appears to form a large rather than a small angle with respect to the surface normal. In addition two very prominent negative-features were found in the region close to 3000 cm^{-1} . This provides evidence that the alkyl chain(s) are collapsed for the oxidized form of EOB acquiring a more stretched configuration as the EOB is reduced in which the alkyl chain skeleton point normal to electrode surface.

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TABLE I

ASSIGNMENT OF SPECTRAL FEATURES OF THE POTENTIAL DIFFERENCE FOURIER TRANSFORM INFRARED SPECTRA OF N-ETHYL-N'-OCTADECYL-4,4'-BYPYRIDINIUM, EOB AND RELATED COMPOUNDS

Wavenumber (cm ⁻¹)		MODEL A Reorientation		MODEL B Vibronic Coupling			
In situ FTIRRAS	Solid Phase	Calc. ^o	Assignment	Calc. ^o	Literature Values** FTIR ⁺ RR ⁺⁺	Assignment a _g	
1026(+)	--	1020	b _{3u} ν(C-C)	1039	1029	ν(C-N, C-C)	
1192(+)	1177	1195	b _{3u} δ(C-H) _{ring} , or ν(N-alkyl)	1208	1200 1211	ν(N-alkyl) or δ(C-H) _{ring}	
1335(+)	--	1338	b _{2u} δ(C-H) _{ring}	1359	1340 1341	ν(C-C), δ(C-H) _{ring}	
1508(+)	1508	1487	b _{3u} ν(C-N, C-C)		1509 1511 ^{oo}	ν(C-N), δ(C-H) _{ring}	
1597(+)	--	1595	b _{3u} ν(C-C)		1600 1607 ^{oo}	ν(C-C)	
1640(+)	1637	1630	b _{2u} ν(C-N)	1651	1634 1658	ν(C-C)	
--	831	833	b _{3u} ν(N-alkyl)				
1120(-)	--		ν ₃ SO ₄ ²⁻				
1458(-)	1450		δ _a -CH ₂ -				
2926(-)	2918		ν _a -CH ₂ -				
2854(-)	2849		ν _s -CH ₂ -				

* The sign in parenthesis indicates whether the feature in the spectrum is positive-, (+), or negative-, (-), going.

o Values quoted are taken from the normal coordinate analysis reported in Ref. 9, for DMB²⁺ (MODEL A) and for DMB⁺ in the case of MODEL B.

** FTIR and Resonant Raman, RR data for (DMB⁺)₂ and N-hexadecyl-N'-methyl bipyridyl radical cations in aqueous media, respectively.

+ From Ref. 10.

++ From Ref. 7.

oo These bands have been associated with dimeric forms of the radical cations (see Ref. 7).

FIGURE CAPTIONS

- Fig. 1. Cyclic voltammetric curves obtained for a self-assembled layer of EOB (prepared in the fashion described in the experimental section) in a solution 0.5 M Na_2SO_4 at different scan rates. A. 50, B. 200, and C. 1000 $\text{mV}\cdot\text{s}^{-1}$. Inset: Molecular structure of EOB.
- Fig. 2. Series of potential difference FTIRRAS spectra obtained in the potential range in which EOB changes redox state in a solution 0.5 M Na_2SO_4 , using the spectrum recorded at -0.30 V vs SCE as a reference.
- Fig. 3. Same spectra as those shown in Figure 2, in the region between 1100 and 2000 cm^{-1} , shown in an expanded form.
- Fig. 4. Comparison of the -0.65 V FTIRRAS spectrum in Figure 2 (Curve A) with that obtained by coadding alternate spectra recorded at -0.3 V and -0.65 V (Curve B), under the same conditions given in Caption Figure 2.
- Fig. 5. FTIRRAS spectrum of adsorbed EOB at -0.3 V obtained by stepping the potential to +1.5 V, holding it at this value for 30 min. and then returned to -0.3 V, using the spectrum at -0.3 V before the step as a reference.











